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DEPARTMENT OF INTEGRATIVE BIOLOGY BERKELEY, CALIFORNIA 94720-3140

24 March 2017

Mr. Daniel McClure
Central Valley Regional Water Quality Control Board
11020 Sun Center Dr., Suite 200
Rancho Cordova, CA 95670-6114

Dear Mr. McClure:

I would like to provide some comments on "Proposed Amendments to the Water Quality Control Plan for the Sacramento River and San Joaquin River Basins for the Control of Pyrethroid Pesticides Discharges". As a faculty member at UC Berkeley, I have worked almost exclusively on pyrethroid toxicology since 2003, and on other compounds with similar chemical properties for 20 years before that. My pyrethroid research has focused largely on documenting their presence and toxicity in many Region 5 waterbodies, development of techniques to determine if pyrethroids are responsible for observed toxicity, determining their bioavailability, and documenting genetic mutations that are appearing in wild populations of invertebrates chronically exposed to them.

I will note at the outset that I am sympathetic to the difficulties that confront Region 5 staff in controlling pyrethroid discharges. Among those challenges, pyrethroids cause sublethal toxic effects below concentrations we can even measure in the environment. Pyrethroid contamination, and its associated toxicity, is so pervasive that it exists in nearly all urban runoff and a substantial fraction of agricultural and POTW discharges. There are jurisdictional considerations, with potential Region 5 options constrained by the regulatory responsibilities of DPR and EPA's Office of Pesticide Programs. Given all this, I acknowledge that Region 5 staff face considerable challenges.

As a scientist, however, I feel it is my obligation to try and insure regulatory actions fully and appropriately utilize available scientific knowledge, and can withstand challenges to the science that underlies them. The approach staff has used to address the bioavailability of pyrethroids, and to regulate only what they view as the bioavailable fraction, fails on both these counts.

Very briefly, staff propose: 1) quantifying the total pyrethroids in a water sample; 2) using literature-derived values for K_{oc} and K_{doc} to mathematically discount the pyrethroid that may be bound to particles or dissolved organic matter; 3) placing regulatory limits only on the remaining "freely dissolved" fraction of the pyrethroid, usually likely to be <10% of the total; and 4) placing no limits on the remaining ~90% of pyrethroid in water samples, presuming it to be not bioavailable to organisms. There are numerous serious problems with such an approach:

Novelty – The proposed approach is not common or well validated, in fact, this is actually the first time it has ever been used in a regulatory context. Certainly there are many papers in the scientific literature that discuss partitioning of pyrethroids among the various pools (dissolved, particulate, etc.), but I am not aware of any prior regulatory application of the theory, or attempts to only place limits on only the "bioavailable" freely dissolved fraction. I have checked with European collaborators, and they are aware of none there either. While the first use of a regulatory approach does not inherently make it wrong, it does call for a particularly strong and convincing justification to toss aside decades of regulation of the total contaminant concentration, and an explanation for why it has to be done now for pyrethroids when it has never been done for other compounds with very similar chemical properties (e.g., DDT, PCBs). The staff report fails to make the case for applying a unique and untested regulatory approach to pyrethroids, and simply glosses over inherent assumptions that are most certainly wrong.

I cannot help but note that over the past year, as the staff report was under development, dischargers and the pyrethroid manufacturers forcefully and repeatedly argued against use of Hyalella toxicity testing because the methodology has not been standardized (i.e., protocols not yet promulgated by EPA or a similar standard-setting entity). However, these very same stakeholders have no problem accepting the chemical approach of using K_{oc} and K_{doc} values to regulate only the freely dissolved fraction. Not only is the measurement of these parameters not standardized, but their application in a regulatory context has never even been done before! Yet dischargers and pyrethroid manufacturers are quite happy to accept this unstandardized approach without reservation because it removes ~90% of the pyrethroid in the effluent from regulatory limits. This double standard makes their concerns about standardization in toxicity testing appear specious and hypocritical.

Bioavailability of particle-bound contaminant – The association of pyrethroids with suspended particles will reduce bioavailability of the compounds to organisms living in the water column if they do not feed upon those particles. But as contaminants become increasingly particle associated (e.g., pyrethroids, DDT, PCBs, combustion-derived aromatic hydrocarbons), contaminant uptake via ingestion becomes the dominant uptake route for organisms that feed on these particles by filter feeding or deposit feeding. There are dozens of publications, my own included, that show assimilation of such substances via ingestion. A few examples using compounds with hydrophobicity comparable to pyrethroids include:

1) Mussels feeding on suspended algal cells assimilated 98% of the PCB on that material (Chemosphere 36:3181-3197 (1998)).
2) An amphipod feeding on sediments containing benzo(a)pyrene assimilated 46-60% of the ingested contaminant (Chemosphere 26:209-224 (1993)).
3) Hexachlorobenzene assimilation efficiency from ingested particles ranged from 39-57% in a clam, 15-36% in an oligochaete worm, and 53% in a mysid (see previous reference under #2).

Yet despite overwhelming scientific evidence to the contrary, the staff report assumes biological uptake from particle-bound pyrethroids to be zero, or at least negligible, and therefore in no need of regulatory control. Characterization of the particle-bound fraction as non-bioavailable, as done in the staff report, is indefensible. While it may apply to

organisms that do not interact with the particles to which the pyrethroid is adsorbed, and is sometimes used in the scientific literature in this limited context, it is not an accurate characterization for countless filter-feeding and deposit-feeding aquatic species.

I should also note that the exclusion of particle-bound pyrethroids from regulatory limits is likely to be of greatest significance with respect to agricultural discharges, since they often have the highest suspended sediment loads. The proposed approach provides a disincentive for growers to control release of suspended sediments. There is no reason for a grower to reduce suspended sediment discharge, especially if those sediments are coming from untreated areas, since doing so will only increase the likelihood that the grower's pyrethroid releases from treated land will cause a regulatory exceedance. The potential to manipulate suspended sediment so as to avoid a pyrethroid exceedance is akin to simply diluting to meet a treatment standard; neither should be acceptable practice to avoid regulatory limits.

Limited K_{oc} and K_{doc} data – The numerical values assigned to K_{oc} and K_{doc} are critical when employing the staff's recommended approach, but these values are likely to be highly site specific. Since it is not realistic to expect K_{oc} and K_{doc} to be measured by dischargers in every sample, staff expects default literature values to be necessary. Based on staff's quality assurance criteria, they found only a single study, using laboratory water and a sediment from a pond in Massachusetts, to provide acceptable K_{oc} and K_{doc} values for non-POTW waters. Staff recommended that everyone use these default values (e.g., bifenthrin K_{oc} = 4,228,000, K_{doc} = 1,737,127). Simply on the face of it, it is blatantly absurd to expect that a single measurement, derived from one Massachusetts pond, is applicable to every water sample taken anywhere in Region 5, but that is precisely what the staff report advocates.

There are great quantitative and qualitative differences in the amount and type of particulate and organic matter from place to place, and from one time to the next, and thus their potential adsorption of pyrethroids varies tremendously. The staff report fails to provide any sense of how much variation might be expected in the single K_{oc} or K_{doc} it proposes to apply everywhere, and there is good reason to suspect it is likely to be enormous. An earlier version of the staff report used K_{oc} and K_{doc} from other studies that tested multiple sediments, and reported a two order-of-magnitude variation in each of these parameters among the sediments evaluated. The site-to-site variability in K_{oc} and K_{doc} is so great, that a recent literature review on the topic simply concluded such parameters are essentially useless to predict toxicological risk, stating, "the bioavailability and toxicity of pesticides to aquatic organisms in the presence of particles cannot simply be predicted by the partitioning of pesticides between water and particles using the K_{oc}" (Knauer et al., Integ. Environ. Assess. Manage.; Manuscript in press but not yet assigned to a specific issue but available on journal's website.)

In addition, literature K_{oc} and K_{doc} values for pyrethroids are based on clean laboratory waters to which uniform, homogenized, well-characterized particulates or dissolved organics are added. To the best of my knowledge, they have never been measured in any field samples, with all the "messy" particulate and dissolved organic carbon they may contain, yet the proposed approach advocates applying them to field samples throughout Region 5 without validation.

For POTW effluents, the limited data makes the approach even more dubious. The same quality assurance procedures that were used to find almost all existing K_{oc} and K_{doc}

estimates for non-POTWs unsuitable for use in the staff report, were not applied to POTW-related data simply because there was only one study that had generated these values for POTWs. Ironically, that one study is one on which I was the lead investigator, though the pyrethroid partitioning work was done by a subcontractor. Nevertheless, if most of the non-POTW data are unacceptable for use because they did not meet quality assurance standards, why does POTW data with these very same omissions become acceptable? Wouldn't the better answer be acceptable POTW values don't exist, rather than the implied rationale of the staff report as, 'It could be wrong, but it's all we've got, so we'll use it anyway'?

Yet despite the absolute lack of any information on potential site-to-site variability in K_{oc} and K_{doc}, the extraordinarily limited single-site data on which the default values are based, or any demonstration that these values are useful predictors in field situations at all, the proposed approach proposes applying these default values throughout Region 5. On what basis does staff presume that the K_{oc} and K_{doc} values derived from a single pond in Massachusetts apply to every stormwater runoff sample and every agricultural discharge in Region 5? How can a given discharge that attains a final pyrethroid criteria value of 1 be declared compliant, while one that scores a 2 is in exceedance, with all the associated regulatory consequences, when both of two variables used to calculate that score could be off by a factor of 100 or more? The application proposed is not remotely supportable by the current state of knowledge.

RECOMMENDATIONS

I have voiced these concerns repeatedly in the several Board meetings held over the past year, but to no avail. After all, if the proposed TMDL trigger levels are based on an approach: 1) never before used anywhere in the world, 2) that disregards 90% of the pollutant, 3) that incorporates numerical values that have never been shown to be generally applicable or field-verified, and 4) that is not scheduled to be re-assessed by the Board for 15 years, what could possibly go wrong?

As I mentioned initially, the challenges in regulating pyrethroids are immense, and I can accept that some compromises may be necessary because of concerns such as enforceability, feasibility of attainment, or cost. But regulatory approaches based upon these kinds of considerations should be identified as such, not defended as scientifically based. My concern is that once Region 5 adopts the approach, other jurisdictions may be quick to do so as well, with the assumption that Region 5's adoption implies a scientific rigor that is not actually there. Nevertheless, if Region 5 elects to pursue the approach currently in the staff report, despite consideration of my comments and others that may be received, I recommend the following:

1) The use of default K_{oc} and K_{doc} values in a wide variety of water types should receive immediate validation. I do NOT mean compilation and review of the data that dischargers will be gathering as part of their obligations under the TMDL, but a special study to be done in the first couple years after adoption of the TMDL. This study should attempt direct measurement of K_{oc} and K_{doc} in a wide variety of field samples so as to determine whether the proposed laboratory-derived default values have any real world validity, establish the variability of these parameters among samples, determine if perhaps use of a few default

values could be more defensible (e.g., each applied to only a specified range of suspended sediment or dissolved organic carbon concentrations), and assess their value in predicting toxicity. This study should also evaluate the suitability of using Tenax extractions as an alternative to SPME-based default values. It may be possible for commercial laboratories to actually do Tenax-based analyses on many or most samples, avoiding the need for default values all together, and there is evidence that Tenax provides an estimate of toxicological risk that is at least as good if not better than SPMEs (see for examples: Environ. Toxicol. Chem. 20:706-711 (2001); Environ. Sci. Technol. 41:5672-5678 (2007); Environ. Toxicol. Chem. 27:2124-2130 (2008); J. Environ. Monit. 13:792-800 (2011); Environ. Poll. 173:47-51 (2013). Disclosure: I am a co-author on two of these studies.)

2) I would suggest that sampling done both during the initial baseline data collection period under the TMDL, and then to determine compliance for at least the following few years, ALWAYS includes toxicity testing with Hyalella azteca. Given the enormous uncertainties behind the "freely dissolved only" approach being recommended, and the fact that the trigger levels being proposed are nearly the same as the species' LC50s, it is unlikely that compliance with numerical triggers will actually be protective of this species. It is toxicity to this species that led to the current 303(d) listings for pyrethroids, and if the proposed approach does not protect this species, then how can the TMDL ever be expected to eventually lead to de-listing? In addition, Hyalella azteca is a species commonly used to measure toxicity in most toxicity laboratories in Region 5, it is a resident species found throughout Region 5 and all of California, and it is often found in such high abundance as to be the dominant macroinvertebrate. Toxicity to it cannot be lightly dismissed, so it is essential to establish if the proposed triggers are protective.

I should also add that many commercial laboratories only report mortality, yet by their very nature, pyrethroids are neurotoxins that cause paralysis prior to death. When an actively swimming animal is unable to do anything more than lay on the bottom twitching, most reasonable people would consider that an adverse effect that bears noting. Yet because paralysis is not a standardized endpoint, nor is it in the interest of dischargers to document it, many testing laboratories have turned a blind eye to immobility, not reporting it and treating it as if there is no effect at all. Paralysis may be a more subjective endpoint to quantify than death because there can be a gradation in severity, but it is no less environmentally relevant, so I would encourage an effort to standardize and report a paralysis endpoint among laboratories.

3) During Board hearings, staff presented graphs using 108 samples from my prior studies, showing those toxic samples that would have been flagged as exceedances based on their proposed criteria, and those samples that would have been in compliance but were toxic nonetheless. Staff repeatedly insisted that they could not use this kind of analysis to set the criteria, arguing that a toxic sample that was in compliance for pyrethroids, may simply have been toxic due to some other unknown substance. While I personally doubt whether other substances were playing a significant role in toxicity within this data set, I cannot prove that. However, if staff considers data of this type to be unsuitable to set the criteria, as they asserted repeatedly, then it would seem comparable data collected in the coming years would be equally unsuitable to evaluate the criteria. The uncertainly of toxicity due to unknown substances would still remain. Staff have proposed a phased approach, in which

the early years of the TMDL will be used to review the data that are collected to see how well the exceedance threshold identifies the samples found to be toxic. But their past arguments seem to already discount this type of data, since if they argue such data cannot be used to set criteria, then they cannot be used to evaluate them either. Greater consideration to how the appropriateness of the proposed trigger values will be evaluated is needed, since staff seem to have already dismissed the only approach possible with the data being gathered.

4) Greater clarity is needed in the staff report on when an acute criterion (1-hr average concentration), versus a chronic criterion (4-day average concentration), is to be used. In nearly all instances, it is likely that the discharger will have taken only a single grab sample, so an "averaging period" becomes a moot point. The staff report is silent on whether a single grab sample should be viewed as an acute exposure or if it can be assumed to be representative of exposure that lasted many days. Assumption of chronic exposure, that perhaps may be appropriate with a POTW effluent, becomes less clear in, for example, agricultural irrigation runoff. Of particular concern is the last sentence of Appendix B, which explicitly places stormwater runoff within the acute category. My work both in the American River and in Cache Slough has shown elevated pyrethroid concentrations and/or toxicity persisting in these waterbodies for 5 days after a storm, and would certainly best be considered as chronic exposure. In winters such as we have just had, back-to-back rainy periods, and the associated pyrethroid inputs via runoff, can extend over many weeks. I suggest modifying the Appendix B sentence noted, and also providing explicit guidance elsewhere in the staff report.

Thank you for your consideration of these comments and recommendations.

Sincerely,

Donald P Weston

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